2 H diastereotopic), 5.35–5.9 (m, 2 H); NMR (DMSO, 60 MHz) δ 3.73 (s, OH), 3.78 (s, OH); IR (neat) 3500, 3020, 1650, 1005, 985, 975, 960, 915, 890 cm^{-1}; MS is identical with that of diastereoisomer a.

2,6-Dimethyl-1-(1-methyl-2-propenyl)cyclohexanol. GC (DB1, 30 m, 70 °C + 2 deg/min) showed that three isomers were present (a–c). Two of these were obtained in pure form; c was in too little quantity and was collected with 2,6-dimethyl-1-(2-butenyl)cyclohexanol. It was identified by NMR ($CDCl_3$, 300 MHz): δ 4.95–5.05 (m, 2 H), 5.15–6.1 (m (7 lines), 1 H). The eluant was a mixture of pentane–ether, 98/2 v/v. The relative configurations of these isomers are unknown.

Diastereoisomer a: NMR ($CDCl_3$, 300 MHz) δ 0.84 (d, J = 6.6 Hz, 3 H), 0.91 (d, J = 6.6 Hz, 3 H), 1.05 (d, J = 7 Hz, 3 H), 1.2–1.6 (m, 8 H + OH), 2.68 (dq, $J_1 = J_2$ = 7 Hz, 1 H), 5–5.1 (m, 2 H), 5.9–6.05 (m (7 lines), 1 H); IR (neat) 3570, 3075, 1630, 1000, 970, 945, 920 cm^{-1}; MS, 127 (M – 55), 109 (base), 83, 69, 55. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.11; H, 12.25.

Diastereoisomer b: NMR ($CDCl_3$, 300 MHz) δ 0.9 (d, J = 6.6 Hz, 3 H), 1.06 (d, J = 6.6 Hz, 3 H), 1.09 (d, J = 7 Hz, 3 H), 1.2–1.8 (m, 8 H + OH), 2.43 (dq, $J_1 = J_2$ = 7 Hz, 1 H), 5.05–5.15 (m, 2 H), 5.95–6.1 (m (7 lines), 1 H); MS is identical with that of diastereoisomer a.

2,6-Dimethyl-1-(2-butenyl)cyclohexanol. GC (DB1, 30 m, 70 °C + 2 deg/min) showed four isomers (d–g), and these were collected as mixtures. The relative configurations of these isomers are unknown.

Mixture of diastereoisomers d + e: NMR ($CDCl_3$, 300 MHz) δ 0.93 (d, J = 7 Hz, 6 H), 1.66 (dm, 3 H), 1.2–1.8 (m, 8 H + OH), 2–2.5 (m, 2 H diastereotopic), 5.45–5.75 (m, 2 H); IR (neat) 3500, 3020, 1650, 1035, 990, 970, 945, 735 cm^{-1}; MS, 127 (M – 55), 109 (base), 83, 69, 67, 55.

Mixture of diastereoisomers f + g: NMR ($CDCl_3$, 300 MHz) δ 0.89 (d, J = 6.6 Hz, 6 H), 1.2–1.7 (m, 8 H + OH), 1.66 (dm, 3 H), 2.2–2.35 (m, 2 H diastereotopic), 5.2–5.6 (m, 2 H); IR very similar to that of d + e; MS, identical with that of d + e.

Mixture of diastereoisomers d–g. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.94; H, 12.32.

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Azophilic Addition of Alkyllithium Reagents to Fluorenimines. The Synthesis of Secondary Amines

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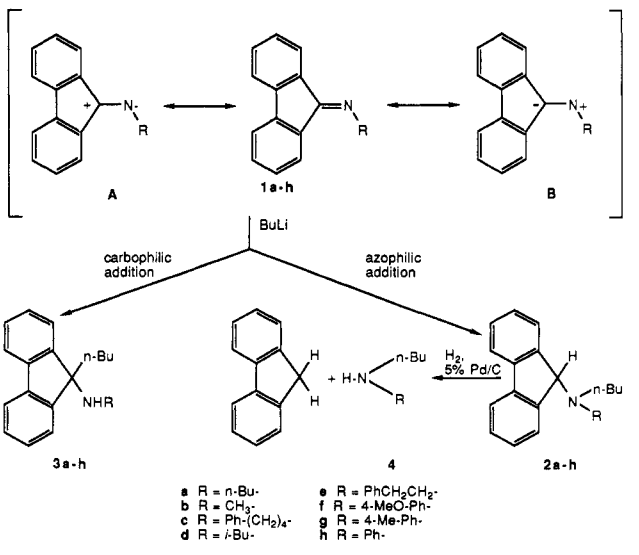
N-Alkyl- and *N*-arylfluorenimines undergo azophilic addition with *n*-BuLi to give *N*-butyl-*N*-alkyl- or *N*-butyl-*N*-aryl-9-aminofluorene systems. The fluorenyl group can then be hydrogenolyzed, furnishing the secondary amine. The selectivity for azophilic (vs carbophilic) addition ranges from 80 to 100% for the *N*-alkylfluorenimines to 24–29% for the *N*-arylfluorenimines. The decreased azophilic selectivity of the *N*-arylfluorenimines can be rationalized on the basis of frontier molecular orbital interactions as well as steric effects. Other related imines, that would appear to provide an inverse polarization similar to that of the fluorenimines, do not give satisfactory yields of azophilic addition products.

Introduction

It is well known that most organometallic addition reactions to carbon–nitrogen double bonds proceed with a nucleophile attacking on carbon (carbophilic addition). Even though there are a few reports of nucleophile attack on certain electrophilic nitrogen derivatives, such as oximes[1] or oxime tosylates,[2,3] nucleophilic addition to the nitrogen end of a carbon–nitrogen double bond (azophilic addition) has been mentioned only rarely.[3-5,6] For example, Metalova[5] reported that the reaction of *N,N'*-diphenyl-*p*-quinone (I) with MeLi or PhLi gave the product of azophilic 1,6-addition in 27–53% yield, and Murdoch[3] observed that *N*-alkyltetraphenylcyclopentadienimines (II) underwent reaction with aliphatic lithium and Grignard

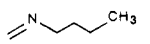
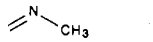
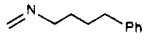
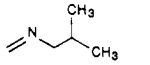
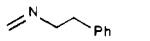
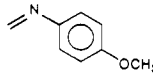
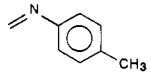
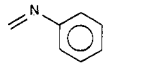
Scheme I



(1) Laurent, A.; Alvernhe, G. *Tetrahedron Lett.* **1972**, *11*, 1007.
(2) Fleury, J. P.; Perchaise, J. *Tetrahedron* **1974**, *30*, 999.
(3) Murdoch, J. R.; Hagopian, R. A.; Therien, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 5753.
(4) Rieker, A.; Bracht, J. *Synthesis* **1977**, 708.
(5) Metalova, M.; Honzl, J. *Tetrahedron* **1969**, *25*, 3641.
(6) There are, of course, many examples of organometallic additions on nitrogen in nitrogen–nitrogen multiply bonded systems. See, for example a–i. (a) Smith, P. A. S.; Rowe, C. D.; Bruner, L. B. *J. Org. Chem.* **1969**, *34*, 3430. (b) Trost, B. M.; Pearson, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 2483. (c) Hassner, A.; Munger, P.; Belinka, B. J., Jr. *Tetrahedron Lett.* **1982**, *23*, 669. (d) Reed, J. N.; Snieckus, V. *Tetrahedron Lett.* **1983**, *24*, 3795. (e) Trost, B. M.; Pearson, W. H. *J. Am. Chem. Soc.* **1983**, *105*, 1054. (f) Gennari, C.; Colombo, L.; Bertolini, G. *J. Am. Chem. Soc.* **1986**, *108*, 6394. (g) Evans, D. A.; Britton, T. C.; Dorow, R. L.; Dellaria, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 6395. (h) Trimbie, L. A.; Vederas, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 6397. (i) Demers, J. P.; Klaubert, D. H. *Tetrahedron Lett.* **1987**, *28*, 4933.

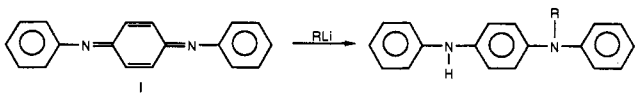
0022-3263/89/1954-2204$01.50/0

Table I. Yields of *n*-Butyllithium Addition Products of Fluorenimines

1		yield % (% by ^{1}H NMR)[a] 2 (azophilic)	3 (carbophilic)	azophilic selectivity,[b] %
a		70 (91)	0 (0)	100
b		71 (90)	0 (trace)	100
c		62 (83)	0 (15)	85
d		41 (64)	0 (16)	80
e		50 (76)	5 (14)	84
f		19 (28)	47 (70)	29
g		17 (22)	52 (71)	24
h		15 (23)	50 (69)	25

[a] Yields after isolation by chromatography on neutral alumina. Yields in parentheses are estimated by ^{1}H NMR analysis of mixtures containing only 2 and 3. [b] Calculated as % 2/(% 2 + % 3), from ^{1}H NMR yields.

reagents to give azophilic addition products (no yields were reported).



I

II

In this report, we present a study of the regioselectivity of alkyllithium addition to fluorenimines (1, Scheme I): This addition proceeds in good yield with an azophilic selectivity that ranges from high (ca. 100%) for alkylimino substituents to moderate (ca. 24%) for aryl substituents. This selectivity can be rationalized on the basis of the relative size of the coefficients of the LUMO on the carbon and nitrogen atoms of the fluorenimine system and the steric effects in the transition state for azophilic addition. The azophilic addition products (2; *N,N*-dialkyl- or *N*-alkyl-*N*-arylfluorenylamines) can be conveniently hydrogenolyzed to secondary amines (4).

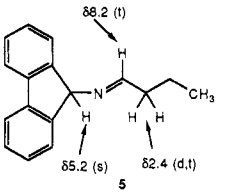
Results and Discussion

Azophilic Addition to Fluorenimines. The fluorenimines (**1a–h**) used in this study and the yields of the alkyllithium addition reactions are shown in Table I. The imines are prepared conveniently in >90% yield by the condensation of fluorenone and the corresponding primary amine with titanium tetrachloride.[7]

The alkyllithium addition reactions proceeded smoothly in THF at −78 to 0 °C and are quite clean, yielding in each case only the two addition products **2** and **3** in greater than 80% yield. The selectivity for azophilic addition is very sensitive to the substituent R. With less hindered substituents (**1a–c**), azophilic addition occurred exclusively, whereas when R is more hindered (**1d** and **1e**), normal (carbophilic) addition begins to compete with azophilic addition. With *N*-aryl imines (**1f–h**), the azophilic addition selectivities are lower; as discussed below, the aryl substituent diminishes the inverse polarizing effect of the fluorenyl group and sterically hinders the transition state for azophilic addition.

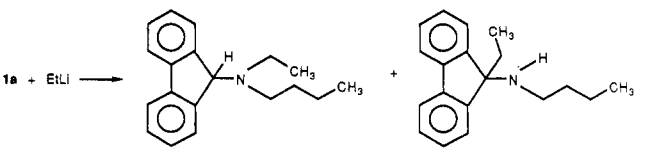
^{1}H NMR analysis provides a convenient method to determine the relative proportion of azophilic product **2** (δ 4.9–5.0 (s) R = Aliph; δ 5.7–5.9 (s) R = Ar; for fluorenyl H-9), carbophilic product **3** (δ 2.0–2.2 (m) for CH_2 attached at fluorenyl C-9), and starting material (δ 3.9–4.4 (s or d or t) for $=NCH_2$ (or 3) R = Aliph; δ 7.9 for fluorenyl H-1 R = Ar), and fluorenone (δ 7.65 (d) or 7.5 (m)).

With respect to the nucleophilic component, the scope of this reaction appears to be relatively narrow: Reaction of **1a** with methyllithium or phenyllithium gave only a mixture of starting material and the nonconjugated imine isomer **5**; methyllithium reaction with **1f** gave only the



5

carbophilic addition product. Ethyllithium reaction with **1a**, however, proceeded as did *n*-butyllithium addition, to give a product mixture (**6** and **7**), consisting mainly of the azophilic addition product (azophilic selectivity 87%). Treatment of **1d** with butyl and phenyl Grignard reagent gave no reaction; the cuprate (Bu_2Cu^-) reagent derived from butyllithium also gave no reaction with the fluorenimine **1a**.



6
65%
(81%, by ^{1}H NMR)

7
5%
(12%, by ^{1}H NMR)

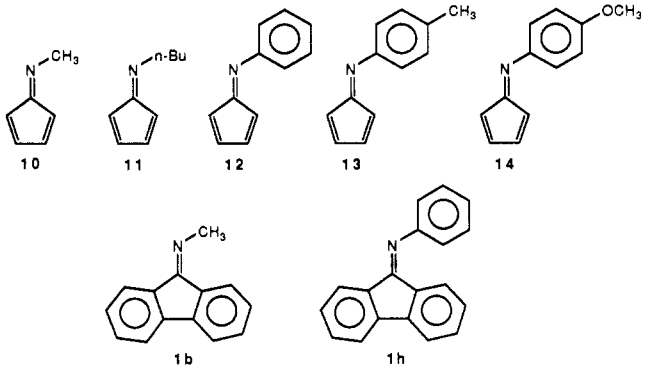
The secondary amines **4** can be obtained from the azophilic addition products **2** by hydrogenolytic cleavage of the fluorene moiety over Pd (5% on carbon) in EtOH in a Parr hydrogenator under 50 psi of hydrogen. In the two examples tried, **2e** and **2f**, the isolated yields after cleavage were 80% and 56%, respectively.

In addition to the fluorenyl systems, we studied two other activating systems. Imine **8** was selected because 2,3-diphenylindene has a lower pK_a (17.7)[8] than fluorene (23),[9] and hence might be yet more activating of imines toward azophilic addition than the fluorenyl substituent; imine **9** was selected because the methyl substituent might hinder, selectively, carbophilic addition. The reaction of imine **8** with butyllithium gave a mixture that included some azophilic addition products, but the selectivity was much lower than with imine **1a**. Imine **9** underwent re-

(7) Weingarten, H.; Chupp, J. P.; White, W. A. *J. Org. Chem.* **1967**, *32*, 3246.

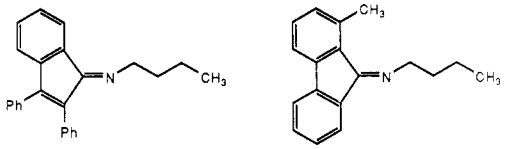
(8) Bordwell, F. G.; Drucker, G. E. *J. Org. Chem.* **1980**, *45*, 3325.
(9) Streitwieser, A., Jr.; Ciuffarin, E.; Hammons, J. H. *J. Am. Chem. Soc.* **1967**, *89*, 63.

Table II. LUMO Coefficients of the C=N Unit and the Fourier Orbital Energies for Imines 10–14, 1b, and 1h



compd	N	C	energy, eV
10	0.486 37	−0.332 15	−0.633 01
11	0.487 16	−0.327 11	−0.606 10
12	0.439 18	−0.379 14	−0.940 73
13	0.435 47	−0.370 42	−0.925 44
14	−0.437 33	0.368 14	−0.905 51
1b	0.375 87	−0.262 68	−0.715 54
1h	0.383 59	−0.305 00	−0.850 18

action with butyllithium to give a series of adducts, without evidence of azophilic addition (no ^{1}H NMR signal at δ 4.9).



Frontier Molecular Orbital Analysis of the Selectivity of Azophilic Addition to Fluorenimine Systems. In their reaction with *n*-butyllithium, N-substituted fluorenimines behave as ambident electrophiles reacting either at the imine nitrogen to give azophilic products or at the imine carbon to give carbophilic products. Thus, *N*-alkylfluorenimines form products derived predominantly from azophilic addition, while *N*-arylfluorenimines favor carbophilic addition. The differing regioselectivity observed in these reactions can be analyzed by perturbation theory.

The reaction between a nucleophile and an electrophile involves a mixing of the occupied orbitals on the nucleophile with the unoccupied orbitals on the electrophile. The most important interaction, however, is that between the LUMO (lowest unoccupied molecular orbital) of the electrophile and the HOMO (highest occupied molecular orbital) of the nucleophile. The energy stabilization (ΔE) of the transition state, gained by mixing of orbitals is given as[10]

$$\Delta E = \left\{ \underbrace{\frac{Q_{nuc}Q_{elec}}{\epsilon R}}_{A} + \underbrace{\frac{2(C_{nuc}C_{elec\beta})^2}{E_{HOMO} - E_{LUMO}}}_{B} \right\}$$

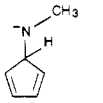
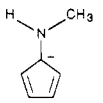
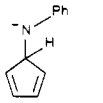
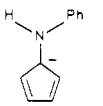
where C_{nuc} is the HOMO coefficient on the nucleophilic site; C_{elec} is the LUMO coefficient on the electophilic site; β is the resonance integral, and $E_{HOMO} - E_{LUMO}$ is the energy gap between the HOMO of the nucleophile and LUMO of the nucleophile; Q_{nuc} and Q_{elec} are the electron populations in the atomic orbitals on the nucleophile and electrophile respectively, ϵ is the local dielectric constant, and R is the distance between the nucleophile and electrophile. Term A in the above equation is the electrostatic contribution to the stabilization of the transition state, while term B represents the frontier molecular orbital (FMO) contribution. While the electrostatic contribution has been shown to be important in deciding regioselectivity in some cases, the frontier orbital term is probably the deciding factor in this reaction. We have therefore chosen to consider only the frontier molecular orbital contribution.

(10) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; J. Wiley: New York, 1976; pp 27 and 37.

Table III. Fourier Orbital Interaction Energies for Azophilic or Carbophilic Addition of Butyllithium to Imines 10–14, 1b, and 1h

compd	ΔE_{azo}, eV	ΔE_{carbo}, eV	$\Delta E_N - \Delta E_C$, eV
10	−4.740 308 4	−2.516 470 3	−2.223 910 1
11	−4.727 710 7	−2.426 269 0	−2.301 441 7
12	−4.145 789 3	−3.384 632 7	−0.761 156 6
13	−4.061 388 3	−3.344 953 0	−0.716 435 3
14	−4.077 052 1	−3.288 496 7	−0.788 055 4
1b	−2.883 490 9	−1.603 011 4	−1.280 479 5
1h	−3.096 527 6	−2.155 889 8	−0.940 362 8

Table IV. Heats of Formation for Anions That Result from Carbophilic vs Azophilic Addition

anion system	ΔH_f, kcal/mol	$\Delta\Delta H_f$, kcal/mol
	66.42	45.13
	21.29	
	71.36	21.84
	49.52	

The regioselectivity of a reaction can be predicted by a comparison of the values of ΔE for attack at each site: The site for which the greatest stabilization of the transition state is afforded (ΔE is most highly negative) is the preferred site of attack. We have evaluated the values of ΔE using the AM1 method.[11]

For our calculations, we have considered molecules **10**–**14**, **1b**, and **1h**. In order to reduce the time of computation, we have approximated the fluorenyl system by a cyclopentadienyl system. To verify that the conclusions drawn from this system are applicable to the fluorenyl system, we have also performed AM1 calculations on two of the experimentally studied systems, **1b** and **1h**. These structures were fully optimized by the AM1 method and by constraining the cyclopentadienyl and fluorenyl portions of the molecules to be planar. The LUMO energies and the coefficients on the imine nitrogen and imine carbon are summarized in Table II.

The energy of the HOMO of *n*-BuLi was calculated to be −5.178 621 eV. The resonance integral β was assumed to have a value of 5.83 for a C–N bond and 6.22 for a C–C bond.[12] Using these parameters, we evaluated the energy stabilization for attack at the two sites (cf. Table III). As is evident from Table III, attack at nitrogen is favored over

(11) Dewar, M. J. S.; Zoebisch, E. G.; Healey, E. F.; Steward, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.

(12) β is a distance-dependent parameter, and the values used in this case are those for a distance of 1.75 Å. Calculations assuming a value of 2.0 Å lead to the same conclusions. For a tabulation of β values based on a CNDO/2 procedure see Houk, K. N.; Sims, J.; Duke, R. E.; Strozier, R. W.; George, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7287.

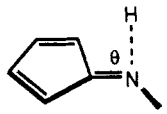


Figure 1. Dependence of energy on angle of hydride approach to the cyclopentadienimine system, as shown in the text.

attack at carbon in all cases ($\Delta E_N - \Delta E_C < 0$). Also, the preference for attack at nitrogen is greater when the N-substituent is alkyl (**10**, **11**, **1b**) than when the substituent is aryl (**12**, **13**, **14**, **1h**). Both of these calculation results are consistent with our experimental findings (cf. Table I).

It should also be noted that azophilic attack would generate an anion centered on carbon, which could then become part of an aromatic system (cf. Scheme I). The AM1 heats of formation of the various anions are shown in Table IV.

Again, anion product stabilities parallel the regioselectivity assigned by the frontier orbital considerations. The extent to which the anion intermediates derived from azophilic addition is formed is much larger in the case of the methyl-substituted nitrogen than in the *N*-phenyl case.

Steric interaction may also account for the decreased selectivity for azophilic addition in the case of the *N*-phenylimines. The optimized geometry of N-Ph imines show the phenyl ring to be at an angle of 43° from the plane of the cyclopentadiene ring.

In order to evaluate the optimal angle for the approach of the nucleophile (i.e, the trajectory of the nucleophile), a H^- was placed at 2.0 Å from the nitrogen, perpendicular to the plane of the cyclopentadienimine. The angle that the H^- makes with the C=N bond was then varied from 90° to 120°, and the heats of formation were evaluated by AM1. The optimal angle was fond to be ~109° (cf. Figure 1). Thus, even though the nitrogen would be pyramidalizing in the transition state, there could be considerable steric interaction between an approaching nucleophile and the aryl ring on the imine nitrogen.

Thus, a consideration of both reactant and product characteristics clearly favors azophilic addition, as long as a soft–soft (FMO) interaction is involved.

Conclusions

Certain imines derived from fluorenone can undergo addition reactions with butyllithium that are regiochemically inverted from the normal sense: azophilic rather than carbophilic. The selectivity for azophilic addition is greatest when the substituent is unhindered and aliphatic, somewhat lower with more hindered aliphatic imine systems, and lowest with aromatic groups. The tertiary fluorenylamine products can be converted to secondary amines by catalytic hydrogenolysis of the fluorenyl group over palladium on carbon at medium pressure. The azophilic selectivity can be rationalized by frontier molecular orbital considerations, which predict a higher azophilic selectivity for the *N*-alkyl than the *N*-aryl systems. This selectivity is also expected on the basis of steric interactions in the transition state, and it parallels the relative heats of formation of the anion intermediates.

Experimental Section

General. All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. The proton nuclear magnetic resonance spectra (^{1}H NMR) were measured with a Varian spectrometer Model XL-200. The values are reported on the δ scale with reference to internal Me_3SiCl, using $CDCl_3$ as solvent. High-resolution mass spectra were determined with a Varian spectrometer, Model MAT 731.

Ethyllithium was obtained from Organometallics, Inc. All other chemicals were purchased from Aldrich. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Toluene and the amines used were purified by refluxing with CaH_2, followed by distillation. Other chemicals were used as received.

General Procedure for Synthesis of Fluorenimines 1. To a well-stirred solution of fluorenenone (15.0 mmol, 2 equiv) and corresponding amine (67.0 mmol, 9 equiv) in dry toluene (100 mL) under N_2 at 0 °C was added dropwise $TiCl_4$ (11.3 mmol, 1.5 equiv) over a period of 1 h. The dark brown reaction mixture was stirred at 25 °C for 1 h and then warmed to 100–110 °C overnight. After being cooled to 10 °C, the reaction mixture was diluted with ether (150–200 mL) and was stirred until the color of the precipitate totally changed to light yellow. The mixture was filtered through Celite, and the collected precipitate was washed with ether. Concentration of the combined filtrate and washes gave the fluorenimine in good yield.

***N*-Butylfluorenimine (1a)**: yield 98%; yellow oil; ^{1}H NMR δ 1.40 (t, 3 H, J = 8 Hz, CH_3), 1.68 (m, 2 H, $MeCH_2$), 1.92 (m, 2 H, CH_2), 4.15 (t, 2 H, J = 8 Hz, NCH_2), 7.23–7.92 (m, 8 H, Ar); HRMS calcd for $C_{17}H_{17}N$ m/e 235.1361, found m/e 235.1364.

***N*-Methylfluorenimine (1b)**: yield 97%; yellow crystals; mp 47–48 °C; ^{1}H NMR δ 3.59 (s, 3 H, NCH_3), 7.25–7.93 (m, 8 H, Ar); HRMS calcd for $C_{14}H_{11}N$ m/e 193.0891, found m/e 193.0892.

***N*-(4-Phenylbutyl)fluorenimine (1c)**: yield 92%; viscous brown oil; ^{1}H NMR δ 1.95 (m, 4 H, 2 CH_2), 2.74 (t, 2 H, J = 7 Hz, $PhCH_2$), 4.14 (t, 2 H, J = 7 Hz, NCH_2), 7.13–7.88 (m, 13 H, Ar); HRMS calcd for $C_{23}H_{21}N$ m/e 311.1674, found m/e 311.1669.

***N*-Isobutylfluorenimine (1d)**: yield 95%; yellow crystals; mp 40–41 °C; ^{1}H NMR δ 1.12 (d, 6 H, J = 7 Hz, 2 CH_3), 2.20 (m, 1 H, Me_2CH), 3.92 (d, 2 H, J = 7 Hz, NCH_2), 7.22–7.90 (m, 8 H, Ar); HRMS calcd for $C_{17}C_{17}N$ m/e 235.1361, found m/e 235.1365.

***N*-Phenethylfluorenimine (1e)**: yield 95%; yellow crystals; mp 62–63 °C; ^{1}H NMR δ 3.28 (t, 2 H, J = 9 Hz, $PhCH_2$), 4.49 (t, 2 H, J = 9 Hz, NCH_2), 7.20–7.93 (m, 13 H, Ar); HRMS calcd for $C_{21}H_{17}N$ m/e 283.1361, found m/e 283.1356.

***N*-(4-Methoxyphenyl)fluorenimine (1f)**: yield 91%; brown crystals; mp 134–135 °C; ^{1}H NMR δ 3.87 (s, 3 H, OCH_3), 6.78–7.95 (m, 12 H, Ar); HRMS calcd for $C_{20}H_{15}NO$ m/e 285.1154, found m/e 285.1148.

***N*-(4-Methylphenyl)fluorenimine (1g)**: yield 90%; yellow crystals; mp 116–117 °C; ^{1}H NMR δ 2.41 (s, 3 H, $PhCH_3$), 6.60–7.95 (m, 12 H, Ar); HRMS calcd for $C_{20}H_{15}N$ m/e 269.1205, found m/e 269.1203.

***N*-Phenylfluorenimine (1h)**: yield 93%; dark yellow crystals; mp 83–84 °C; ^{1}H NMR δ 6.50–7.95 (m, Ar); HRMS calcd for $C_{19}H_{13}N$ m/e 255.1048, found m/e 255.1043.

General Procedure for the Reaction of Fluorenimines with Alkyllithiums. To a stirred solution of *n*-BuLi (1.6 M in hexane, 1.1 mmol) (or EtLi 1.4 M in PhH, 1.1 mmol) in THF (5 mL) was slowly added a solution of a fluorenimine (1 mmol) in THF (5 mL), at −78 °C under N_2. After the mixture was stirred for 2 h, the temperature was slowly raised to 0 °C, and the stirring was continued for another 10 min. The reaction mixture was then quenched with ice water (10 mL), extracted with ether, and dried over Na_2SO_4. The ^{1}H NMR yields were determined on this crude product. The separation of azophilic and carbophilic adducts was performed by flash column chromatography over neutral alumina (hexane–Et_2O, 9:1).

***N*,*N*-Dibutyl-9-aminofluorene (2a).** This product was obtained by the reaction of BuLi with *N*-butylfluorenimine (**1a**) as a yellow oil in 70% yield: ^{1}H NMR δ 0.83 (t, 6 H, J = 7 Hz, 2 CH_3) 1.23–1.50 (m, 8 H, 4 CH_2), 2.48 (t, 4 H, J = 7 Hz, 2 NCH_2), 4.95 (s, 1 H, NCH), 7.22–7.70 (m, 8 H, Ar); HRMS calcd for $C_{21}H_{21}N$ m/e 293.2143, found m/e 293.2145.

***N*-Methyl-*N*-butyl-9-aminofluorene (2b).** This product was obtained by the reaction of BuLi with *N*-methylfluorenimine (**1b**) as a yellow oil in 71% yield: ^{1}H NMR δ 0.90 (t, 3 H, J = 7 Hz, CH_3), 1.25–1.61 (m, 4 H, CH_2CH_2), 2.17 (s, 3 H, NCH_3), 2.60 (t, 2 H, J = 7 Hz, NCH_2), 4.98 (s, 1 H, NCH), 7.22–7.70 (m, 8 H, Ar); HRMS calcd for $C_{18}H_{21}N$ m/e 251.1674, found m/e 251.1682.

***N*-Butyl-*N*-(4-phenylbutyl)-9-aminofluorene (2c).** The azophilic product **2c** was obtained by the reaction of BuLi with *N*-(4-phenylbutyl)fluorenimine (**1c**) as a yellow oil in 62% yield: ^{1}H NMR δ 0.83 (t, 3 H, J = 7 Hz, CH_3), 1.23–1.65 (m, 10 H, 5 CH_2), 2.52 (m, 4 H, 2 NCH_2), 4.94 (s, 1 H, NCH), 7.09–7.70 (m,

13 H, Ar); HRMS calcd for $C_{27}H_{31}N$ m/e 369.2456, found m/e 369.2448. The carbophilic product **3c** was detected by ^1H NMR spectroscopy but was not easily isolated in adequate quantity for full characterization.

***N*-Butyl-*N*-isobutyl-9-aminofluorene (2d).** The azophilic product **2d** was obtained by the reaction of BuLi with *N*-isobutylfluorenimine (**1d**) as a yellow oil in 41% yield: ^1H NMR δ 0.80 (t, 3 H, J = 7 Hz, CH_3), 0.87 (d, 6 H, J = 7 Hz, $C(CH_3)_2$), 1.21–1.52 (m, 4 H, CH_2CH_2), 2.28 (d, 2 H, J = 7 Hz, NCH_2), 2.42 (t, 2 H, J = 7 Hz, NCH_2), 7.21–7.70 (m, 8 H, Ar); HRMS calcd for $C_{21}H_{27}N$ m/e 293.2143, found m/e 293.2145. The carbophilic product **3d** was detected by ^1H NMR but was not easily isolated in adequate quantity for full characterization.

***N*-Butyl-*N*-(2-phenylethyl)-9-aminofluorene (2e) and *N*-(2-Phenylethyl)-9-butyl-9-aminofluorene (3e).** The azophilic product **2e** was obtained by the reaction of BuLi with *N*-phenethylfluorenimine (**1e**) as a yellow oil in 50% yield: ^1H NMR δ 0.80 (t, 3 H, J = 7 Hz, CH_3), 1.08–1.42 (m, 4 H, CH_2CH_2Me), 2.45 (t, 2 H, J = 7 Hz, NCH_2), 2.70 (m, 4 H, $PhCH_2CH_2$), 4.82 (s, 1 H, NCH), 6.92–7.60 (m, 13 H, Ar); HRMS calcd for $C_{25}H_{27}N$ m/e 341.2144, found m/e 341.2135.

***N*-Phenethyl-9-butyl-9-aminofluorene (3e).** The carbophilic product **3e** was isoalted as a yellow oil in 5% yield: ^1H NMR δ 0.56 (t, 3 H, J = 7 Hz, CH_3), 0.76–0.99 (m, 4 H, $MeCH_2CH_2$), 1.30 (b, 1 H, NH), 1.89 (m, 2 H, NCR_2CH_2), 2.20–2.60 (m, 4 H, NCH_2CH_2Ph), 6.58–7.60 (m, 13 H, Ar); HRMS calcd for $C_{25}H_{27}N$ m/e 341.2144, found m/e 341.2140.

***N*-Butyl-*N*-(4-methoxyphenyl)-9-aminofluorene (2f) and *N*-(4-Methoxyphenyl)-9-butyl-9-aminofluorene (3f).** The azophilic product **2f** was obtained by the reaction of BuLi with *N*-(4-methoxyphenyl)fluorenimine (**1f**) as a yellow oil in 19% yield: ^1H NMR δ 0.67 (t, 3 H, J = 7 Hz, CH_3), 1.05 (m, 2 H, $MeCH_2$), 1.35 (m, 2 H, CH_2), 2.68 (t, 2 H, J = 7 Hz, NCH_2), 3.79 (s, 3 H, OCH_3), 5.75 (s, 1 H, NCH), 6.90 (m, 4 H, $MeOC_6H_4$), 7.20–7.80 (m, 8 H, Ar); HRMS Calcd for $C_{24}H_{25}NO$ m/e 243.1936, found m/e 243.1937.

The carbophilic product (**3f**) was isolated as light yellow crystals: mp 68–69 °C; 47% yield; ^1H NMR δ 0.705 (t, 3 H, J = 7 Hz, CH_3), 0.82 (m, 2 H, $MeCH_2$), 1.10 (m, 2 H, CH_2), 2.02 (m, 2 H, NCR_2CH_2), 3.52 (s, 3 H, OCH_3), 4.17 (b, 1 H, NH), 5.99 and 6.38 (2 m, 4 H, $MeOC_6H_4$), 7.20–7.71 (m, 8 H, Ar); HRMS calcd for $C_{24}H_{25}NO$ m/e 243.1936, found m/e 243.1934.

***N*-Butyl-*N*-(4-methylphenyl)-9-aminofluorene (2g) and *N*-(4-methylphenyl)-9-butyl-9-aminofluorene (3g).** The azophilic product (**2g**) was obtained by the reaction of BuLi with *N*-(4-methylphenyl)fluorenimine (**1g**) as a yellow oil in 17% yield: ^1H NMR δ 0.67 (t, 3 H, J = 7 Hz, CH_3), 1.05 (m, 2 H, $MeCH_2$), 1.32 (m, 2 H, CH_2), 2.29 (s, 3 H, $PhCH_3$), 2.74 (t, 2 H, J = 7 Hz, NCH_2), 5.87 (s, 1 H, NCH), 6.89 and 7.08 (2 m, 4 H, $MeOC_6H_4$), 7.20–7.80 (m, 8 H, Ar); HRMS calcd for $C_{24}H_{25}N$ m/e 327.1987, found m/e 327.1987.

The carbophilic product **3g** was isolated as light yellow crystals: mp 137–138 °C, 52% yield; ^1H NMR δ 0.71 (t, 3 H, J = 7 Hz, CH_3), 0.82 (m, 2 H, $MeCH_2$), 1.11 (m, 2 H, CH_2), 2.00 (m, 2 H, NCR_2CH_2), 2.02 (s, 3 H, $PhCH_3$), 4.35 (b, 1 H, NH), 5.92 and 6.60 (2 m, 4 H, MeC_6H_4), 7.20–7.80 (m, 8 H, Ar); HRMS calcd for $C_{24}H_{25}N$ m/e 327.1987, found m/e 327.1984.

***N*-Butyl-*N*-phenyl-9-aminofluorene (2h) and *N*-Phenyl-9-butyl-9-aminofluorene (3h).** The azophilic product **2h** was obtained by the reaction of BuLi with *N*-phenylfluorenimine (**1h**) as light yellow crystals: mp 64–65 °C; 15% yield; ^1H NMR δ 0.68 (t, 3 H, J = 7 Hz, CH_3), 1.05 (m, 2 H, $MeCH_2$), 1.40 (m, 2 H, CH_2), 2.78 (t, 2 H, J = 7 Hz, NCH_2), 5.93 (s, 1 H, NCH), 6.70–7.80 (m, 13 H, Ar); HRMS calcd for $C_{23}H_{23}N$ m/e 313.1830, found m/e 313.1831.

The carbophilic product **3h** was isolated as light yellow crystals; mp 102–103.5 °C; 50% yield; ^1H NMR δ 0.72 (t, 3 H, J = 7 Hz, CH_3), 0.82 (m, 2 H, $MeCH_2$), 1.10 (m, 2 H, CH_2), 2.00 (m, 2 H, NCR_2CH), 4.45 (b, 1 H, NH), 5.98, 6.46, 6.79 (3 m, 5 H, C_6H_5), 7.20–7.80 (m, 8 H, Ar); HRMS calcd for $C_{23}H_{33}N$ m/e 313.1830, found m/e 313.1834.

***N*-Ethyl-*N*-butyl-9-aminofluorene (6) and *N*-Butyl-9-ethyl-9-aminofluorene (7).** The azophilic product **6** was obtained by the reaction of EtLi with *N*-butylfluorenimine (**1a**) as a yellow oil in 65% yield: ^1H NMR δ 0.84 (t, 3 H, J = 7 Hz, CH_3 of Bu), 1.04 (t, 3 H, J = 7 Hz, CH_3 of Et), 1.32 (m, 2 H, $MeCH_2$), 1.50 (m, 2 H, CH_2), 2.52 (t, 2 H, J = 7 Hz, NCH_2Pr), 2.54 (q, 2 H, J = 7 Hz, NCH_2Me), 4.97 (s, 1 H, NCH), 7.20–7.75 (m, 8 H, Ar); HRMS calcd for $C_{19}H_{23}N$ m/e 265.1830, found m/e 265.1833.

The carbophilic product (**7**) was isolated as a light yellow oil in 5% yield: ^1H NMR δ 0.40 (t, 3 H, J = 7 Hz, CH_3 of Et), 0.74 (t, 3 H, J = 7 Hz, CH_3 of Bu), 1.20 (m, 4 H, $MeCH_2CH_2$), 1.94 (t, 2 H, J = 7 Hz, NCH_2), 2.03 (q, 2 H, J = 7 Hz, NCR_2CH_2Me), 7.20–7.76 (m, 8 H, Ar); HRMS calcd for $C_{19}H_{13}N$ m/e 265.1830, found m/e 265.1827.

General Procedure for the Hydrogenolysis of the Amines. A solution of the amine (0.5 mmol) in ethanol (15 mL) was shaken in a Parr hydrogenator under a hydrogen atmosphere (50 psi) with 5% palladium-on-carbon catalyst (20 mg). After 20 h, the mixture was filtered, and ethanol was removed under vacuum. The white solid was washed with aqueous NaOH (1 N), extracted with ether, and dried over K_2CO_3. Column chromatography on silica gel or neutral alumina (hexane–ether, 1:8) gave the amine.

Butyl(2-phenethyl)amine (4e): obtained as a colorless oil in 80% yield; ^1H NMR δ 0.90 (t, 3 H, J = 7 Hz, CH_3), 1.13 (b, 1 H, NH), 1.30 (m, 2 H, $MeCH_2$), 1.45 (m, 2 H, CH_2), 2.62 (t, 2 H, J = 7 Hz, NCH_2), 3.95 (m, 4 H, $PhCH_2CH_2$), 7.25 (m, 5 H, Ar); HRMS calcd for $C_{12}H_{19}N$ m/e 177.1518, found m/e 177.1515.

Butyl(4-methoxyphenyl)amine (4f): obtained as a colorless oil in 56% yield; ^1H NMR δ 0.95 (t, 3 H, J = 7 Hz, CH_3), 1.43 (m, 2 H, $MeCH_2$), 1.57 (m, 2 H, CH_2), 3.07 (t, 2 H, J = 7 Hz, NCH_2), 3.32 (b, 1 H, NH), 3.75 (s, 3 H, OCH_3), 6.57 and 6.78 (2 m, 4 H, Ar); HRMS calcd for $C_{11}H_{17}NO$ m/e 179.1310, found m/e 179.1315.

Calculations. The coefficients were obtained from optimized AM1 wave functions, with use of the AMPAC (version 1.00) series of programs obtained from QCPE (Bloomington, IN), running on a VAX 11/780 computer. The SYBYL Molecular Modeling package was obtained from Tripos Associates, St. Louis, MO.

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Registry No. **1a**, 59833-09-9; **1b**, 60734-27-2; **1c**, 119437-40-0; **1d**, 62614-04-4; **1e**, 119437-41-1; **1f**, 5455-02-7; **1g**, 10183-83-2; **1h**, 10183-82-1; **2a**, 119437-42-2; **2b**, 119454-90-9; **2c**, 119437-43-3; **2d**, 119437-44-4; **2e**, 119437-45-5; **2f**, 119437-47-7; **2g**, 119437-49-9; **2h**, 119437-51-3; **3e**, 119437-46-6; **3f**, 119437-48-8; **3g**, 119437-50-2; **3h**, 119437-52-4; **6**, 119437-53-5; **7**, 119437-54-6; **10**, 119437-55-7; **11**, 119437-56-8; **12**, 119437-57-9; **13**, 119437-58-0; **14**, 119437-59-1; NH_2-*n*-Bu, 109-73-9; NH_2CH_3, 74-89-5; $NH_2(CH_2)_4Ph$, 13214-66-9; NH_2-*i*-Bu, 78-81-9; $NH_2CH_2CH_2Ph$, 64-04-0; 4-MeOPh-NH_2, 104-94-9; 4-$MePhNH_2$, 106-49-0; NH_2Ph, 62-53-3; BuLi, 109-72-8; EtLi, 811-49-4; fluorenone, 486-25-9.